

Heats of Combustion, Formation, and Isomerization of Ten C₄ Hydrocarbons

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The heats of combustion of ten C₄ hydrocarbons were measured by combustion of the gaseous hydrocarbon in a flame at constant pressure in a glass reaction vessel in a calorimeter. The calorimeter system was calibrated by means of electrical energy.

The experimental data yielded the following values for the standard heat of combustion, $-\Delta H_c^\circ$, at 25° C and constant pressure, of the gaseous hydrocarbon in gaseous oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard reference states, in kcal/mole: *n*-butane, 687.42 ± 0.15 ; 2-methylpropane, 685.37 ± 0.11 ; 1-butene, 649.33 ± 0.18 ; *cis*-2-butene, 647.65 ± 0.29 ; *trans*-2-butene, 646.90 ± 0.23 ; 2-methylpropene, 645.19 ± 0.25 ; 1,2-butadiene, 619.93 ± 0.13 ; 1,3-butadiene, 607.16 ± 0.18 ; 1-butyne, 620.64 ± 0.20 ; 2-butyne, 615.84 ± 0.23 .

Values of heats of isomerization, formation, and hydrogenation were derived from these data.

I. Introduction

The present investigation, sponsored by the U. S. Office of Rubber Reserve, is a continuation of the thermochemical investigation of monomeric compounds [1]² of importance in the national synthetic rubber program, and is also a part of the work of the thermochemical laboratory of this Bureau on the determination of the heats of formation of compounds of importance to industry and science.

Calorimetric measurements have been made of the heats of combustion at constant pressure of *n*-butane, 2-methylpropane (isobutane), 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene (isobutene), 1,2-butadiene, 1,3-butadiene, 1-butyne (ethylacetylene), and 2-butyne (dimethylacetylene).

Values of heats of isomerization, obtained as the differences in the heats of combustion of corresponding isomers, are also reported. Combination of the heats of combustion with the heats of formation of water and carbon dioxide yields values for the heats of formation of these compounds. The description of the determination of the heat of isomerization of 1-3-butadiene to 1,2-butadiene has been previously published [1]. For that determination it was not necessary to determine the electrical energy equivalent of the calorimeter system. The calorimeter system has been calibrated with electrical energy as part of this investigation, thus yielding new values for the heats of combustion of these two compounds.

II. Method

The units of energy, molecular weights, and method of assigning uncertainties are the same as previously described [1].

The relative values of the heats of combustion of these compounds were determined as described previously [1]. This involved the determination of a constant *B* (eq 3 of [1]) from a series of calorimetric

combustion experiments on each compound, where *B* is essentially the temperature rise of the calorimeter system per gram of carbon dioxide formed in the combustion of the hydrocarbon. A standard calorimeter system and approximately the same temperature interval were used in all experiments. The temperature rise was measured as the increase in resistance of the given platinum resistance thermometer as determined on the given resistance bridge.

To determine the absolute values of the heats of combustion of these compounds, it was necessary to determine the electrical energy equivalent *E_s* of the calorimeter system. This was done by using electrical energy to produce the same temperature rise in the standard calorimeter system as was produced in the calorimetric combustion experiments. The experimental value of the heat evolved per mole of hydrocarbon reacting is

$$-\Delta H_c = E_s \cdot B \cdot (44.010)n, \quad (1)$$

where 44.010 is the molecular weight of carbon dioxide, and *n* is the number of moles of carbon dioxide per mole of hydrocarbon (*n* is 4 for these C₄ compounds).

III. Apparatus

1. Calorimeter Systems

The calorimeter assembly, thermometric system, reaction vessel, and sparking system have been described in the paper on the heat of isomerization of the butadienes [1]. Two changes were made in the calorimeter system during the course of this work, necessitating the consideration of three systems, I, II, and III.

The calorimetric combustion experiments on the two butadienes [1] and the two butanes were performed, using system I. After calibration of system I with electrical energy, the Mueller resistance bridge, Number 404, was replaced by a new Mueller resistance bridge, Number 679195. The calorimetric

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² Figures in brackets indicate the literature references at the end of this paper.

combustion experiments on the two butynes were performed, using this calorimeter system II. After calibration of system II with electrical energy, the Picein-coated calorimeter heater [1] was replaced by a new calorimeter heater. The calorimetric combustion experiments on the four butenes and a series of electrical energy calibration experiments were then performed on calorimeter system III. Platinum resistance thermometer No. 262214 was used throughout this investigation.

The Picein on the old Picein-coated heater would occasionally crack, causing electrical leakage; or would chip off, causing a change in heat capacity, therefore, a new heater was made that was completely encased in copper. The new heater was wound on a thin copper cylinder 3 in. in diameter, 3 in. high, and 0.016 in. thick. This cylinder was covered by a sheet of mica, 0.003 in. thick, over which was wound, noninductively, a heater of about 65 ohms of enameled manganin resistance wire, No. 30 AWG. This wire was covered by another sheet of mica and another close-fitting machined copper cylinder, 0.016 in. thick, was slipped over the assembly, and the two copper cylinders were soldered together at the ends (the inner cylinder having been originally machined with a lip at each end so that the two cylinders fitted very closely together at the ends and with just room enough for the wire and the two sheets of mica in the body). A thin copper tube was soldered onto the outer copper cylinder to carry the enameled copper wire leads, No. 28 AWG, through the water in the calorimeter can. The assembled heater was nickel-plated and polished.

2. Apparatus for Measurement of Electrical Energy

The apparatus and arrangement for measuring the electrical energy during the calibration experiments was essentially the same as that described previously [2]. A new Wenner potentiometer (range 0 to 100, 000 μ v), Number 684695, was used to measure the potential drops across the standard resistors. This potentiometer was calibrated by the Resistance Measurements Section of this Bureau immediately preceding this series of experiments, and the potentiometer ratio was determined [3] at the time of each experiment with electrical energy. The potentiometer ratio was determined by connecting in series a 10-ohm standard resistor, a 100-ohm standard resistor, a variable resistance, and an auxiliary battery. The current through this circuit was adjusted, by use of the variable resistance, so that the potential drop across the 100-ohm standard resistor was equal to the emf of the standard cell. This comparison was made by first adjusting the potentiometer working current, using the standard cell, then replacing the standard cell with the potential leads from the standard resistor. When these were equal, the potential drop across the 10-ohm standard resistor was read on the potentiometer. The ratio of this reading to the true potential drop, as calculated from the known current flowing through the standard resistors, is the potentiometer ratio.

The standard cell and standard resistors used were

calibrated by the Electrochemistry Section and Resistance Measurements Section of this Bureau, respectively, at intervals of about 1 year.

The electrical power was computed as the product of the potential drop per ohm across a 0.1-ohm standard resistor in series with the calorimeter heater and the potential drop across the calorimeter heater, corrected for the current through the standard resistors in parallel with the calorimeter heater. The potential drop across the latter was determined from the potential drop across a 10-ohm standard resistor in series with a 10,000-ohm standard resistor, both of which were in parallel with the heater.

The current was diverted from the external "spill" coil to the calorimeter heater and back again with the use of an automatic switch, [4], which was activated by seconds signals obtained from the Time Section of this Bureau.

IV. Chemical Procedure

1. Purity of the Compounds

The source and purity of the 1,2-butadiene and 1,3-butadiene were previously reported [1].

The 1-butyne and 2-butyne were API-NBS samples purified by the American Petroleum Institute Research Project 6 from material supplied by the American Petroleum Institute Research Project 45 at the Ohio State University, through C. E. Boord. The purities of these two samples were reported [5, 6] as follows, in mole percent: 1-butyne, 99.88 ± 0.07 ; 2-butyne, 99.959 ± 0.038 .

The 2-methylpropene (isobutene) was supplied by the Standard Oil Development Co., through W. J. Sweeney, and had a purity of 99.75 ± 0.10 mole percent, as determined from measurements of the freezing point [7] by A. R. Glasgow, Jr., of this Bureau.

The *n*-butane, 2-methylpropane (isobutane), 1-butene, *cis*-2-butene, and *trans*-2-butene were Research Grade hydrocarbons supplied by the Phillips Petroleum Co. through R. C. Alden and F. E. Frey. The purities of each of these samples, except 1-butene, were determined from measurements of freezing points [7] by A. R. Glasgow, Jr., and A. J. Streiff (of the American Petroleum Institute Research Project 6) as follows, in mole percent: *n*-butane, 99.78 ± 0.08 ; 2-methylpropane (isobutane), 99.88 ± 0.06 ; *cis*-2-butene, 99.74 ± 0.10 ; *trans*-2-butene, 99.32 ± 0.08 . The purity of the 1-butene was reported by the Phillips Petroleum Co., from measurements of freezing points, supplemented by mass spectral analysis, to be 99.88 mole percent.

It is believed that in each case the impurity was predominantly isomeric and present in such small amount that the value of the heat of combustion was not significantly affected.

2. Purity of the Reaction of Combustion

As a check on the purity of the reaction of combustion, both the water and carbon dioxide were collected and the masses determined for most of the experiments. The results of these determinations

are given in table 1, in which are listed, for each substance, the number of experiments, the mean value of the stoichiometric ratio, r , of number of moles of carbon dioxide to the number of moles of water collected multiplied by the factor $b/2a$ (where C_aH_b is the empirical formula of the hydrocarbon), and the standard deviation of the mean. "Blank" corrections to the weights of the carbon dioxide and water absorption tubes were taken into account, insofar as their effect on the ratio r was concerned, in conjunction with the procedure described below (section VI, 2) for determining the "ignition" energy. These ignition-energy experiments were performed in the same manner as the combustion experiments, except that the flame was allowed to burn only about 40 sec. instead of about 20 min. as in the regular combustion experiments. The procedure of handling the tubes and length of time of flushing of the reaction vessel with oxygen were made the same. Any blank corrections to the weights of the absorption tubes due to flushing with oxygen or to the absorption of unburned hydrocarbon in the absorption tubes as the result of any incomplete combustion during the ignition and extinction of the flame, were taken into account in the following manner. The deviation of the ratio r from unity for these short-time ignition experiments was translated into an excess or deficiency in the mass of water collected. This correction was applied to the mass of water collected in the regular combustion experiments in calculating the ratio r given in table 1.

TABLE 1. *Stoichiometric ratios of the masses of carbon dioxide to water formed in the combustion of the hydrocarbons*

Substance	Number of experiments	Mean value of the stoichiometric ratio, r	Standard deviation of the mean
1,3-Butadiene.....	8	1.00024	± 0.00022
1,2-Butadiene.....	6	0.99994	± 0.00019
<i>n</i> -Butane.....	6	.99992	± 0.00009
2-Methylpropane.....	6	.99991	± 0.00005
1-Butyne.....	5	.99952	± 0.00019
2-Butyne.....	4	.99980	± 0.00017
1-Butene.....	5	.99962	± 0.00009
<i>cis</i> -2-Butene.....	4	1.00007	± 0.00014
<i>trans</i> -2-Butene.....	5	0.99984	± 0.00024
2-Methylpropene.....	5	.99956	± 0.00021

The heat effect of any possible incomplete combustion during the ignition or extinction of the flame was taken into account also by the method of determining the ignition energy. With this procedure the heat of combustion was in reality determined from the portion of the combustion when the flame was in a steady state, any constant errors associated with the ignition and extinction of the flame canceling out.

Samples of the products of combustion were analyzed for carbon monoxide, the most likely product of incomplete combustion, by the Gas Chemistry Section of this Bureau [8]. In no case was the total amount of carbon monoxide greater than 0.004 percent of the amount of carbon dioxide formed in the combustion, hence no corrections were applied for this small amount of carbon monoxide.

3. Determination of the Amount of Reaction

For each calorimetric combustion experiment, the amount of reaction was determined from the mass of carbon dioxide formed, taking 1 mole or 44.010 g of carbon dioxide as equivalent to one-fourth mole of these C_4 hydrocarbons. No blank corrections were applied to the weights of the carbon dioxide absorption tubes, since these corrections, if significant, were automatically translated into ignition-energy corrections.

V. Calorimetric Combustion Experiments

1. Procedure

The calorimetric combustion experiments were performed as described in the paper on the heats of isomerization of the butadienes [1]. For each of these different hydrocarbons, it was necessary only to vary the amount of primary oxygen entering the reaction vessel to produce a blue flame with a sharp inner cone to insure complete combustion of the hydrocarbons. The rate of flow of the hydrocarbon was set such as to produce upon combustion the required temperature rise of 4°C in the calorimeter system (equivalent to about 60,000 j of energy) in a period of about 20 min. The secondary oxygen rate was set such that the total oxygen (primary plus secondary) was about 150 percent of that required stoichiometrically for complete combustion.

In the experiments with 2-butyne, which is normally a liquid at room temperature, the vapor was introduced into the calorimeter, using helium as the carrier gas. Any combustible impurities in the helium were removed by passing the helium through a tube packed with copper oxide and maintained at about 600°C , then through separate tubes containing ascarite, magnesium perchlorate, and phosphorous pentoxide. The rate of flow of helium was determined with a bypass flowmeter, and at the proper instant during an experiment, the helium was bubbled through a fritted-glass bubbler into the liquid 2-butyne (at 15°C) and fed directly into the calorimetric reaction vessel.

2. Determination of the "Ignition" Energy

Experiments to determine the energy associated with the ignition and extinction of the flame (ignition-energy experiments [1]) were performed on each compound in the same manner as the regular combustion experiments, except that the flame was allowed to burn for only about 40 sec. The energy contributed by the combustion of the hydrocarbon, as determined from the mass of carbon dioxide collected and an approximate value for the heat of combustion of the hydrocarbon, was subtracted from the total energy liberated in the short-time experiments, to yield the ignition energy.

The mean ignition energies (with their standard deviations) as determined by such experiments were as follows: 1,3-butadiene and 1,2-butadiene,

33.1 ± 2.8 j; *n*-butane, 63.7 ± 3.6 j; 2-methylpropane, 60.0 ± 1.3 j; 1-butyne, 57.2 ± 5.6 j; 2-butyne, 71.8 ± 7.3 j; 1-butene, 51.9 ± 4.2 j; *cis*-2-butene, 46.2 ± 4.4 j; *trans*-2-butene, 48.7 ± 0.2 j; 2-methylpropene, 43.0 ± 2.5 j. The uncertainties in these ignition energies were taken into account in calculating the final uncertainties assigned to the heats of combustion.

3. Results of the Calorimetric Combustion Experiments

The results of the calorimetric combustion experiments are given in table 2, in which are listed for each compound the following quantities: the experiment number; ΔR_c , the corrected temperature rise of the calorimeter expressed in ohms; the mass of carbon dioxide formed; q_g and q_v , the quantities of

heat evolved in addition to that evolved by the standard calorimetric process [1]; q_i , the ignition energy; B , the temperature rise in ohms of the calorimeter system contributed by the standard calorimetric process per gram of carbon dioxide formed; and the mean value of B , together with its standard deviation. The data on 1,3-butadiene and 1,2-butadiene have previously been published [1], and only the mean value of B , together with its standard deviation, are given here. These values differ from the previously published values [1] of B due to the use here of the actual ignition energy instead of the "sparking" energy and due to a change in the calorimeter system between the time of the combustion experiments and the electrical energy experiments necessitated by repairs to the reaction vessel.

TABLE 2. The calorimetric combustion experiments

Compound	Experiment number	ΔR_c	Mass of carbon dioxide	q_g	q_v	q_i	B	Mean value of B with its standard deviation
		Ohms	g	j	j	j	Ohms/g CO ₂	Ohms/g CO ₂
1,3-Butadiene								0.0935614 ± 0.000110
1,2-Butadiene								0.0955293 ± 0.000054
<i>n</i> -Butane	1	0.388961	3.68834	-10.1	-349.5	90.8	0.1059294	0.1059307 ± 0.000054
	2	.391255	3.71225	-15.9	-376.2	77.2	.1059456	
	3	.389682	3.69862	-26.3	-382.3	90.8	.1059158	
	4	.391074	3.71027	-23.5	-361.7	90.8	.1059175	
	5	.390701	3.70800	-31.0	-364.0	63.7	.1059464	
	6	.391245	3.71410	-35.0	-366.1	63.7	.1059294	
2-Methylpropane	1	0.391093	3.72580	-18.9	-426.1	73.5	0.1056154	0.1056143 ± 0.000032
	2	.390330	3.71645	-30.2	-372.2	60.0	.1056250	
	3	.390794	3.72093	-34.5	-362.2	60.0	.1056125	
	4	.390611	3.71728	-21.2	-345.1	60.0	.1056152	
	5	.389206	3.70505	-14.5	-375.1	73.5	.1056003	
	6	.388287	3.69483	-18.0	-356.1	73.5	.1056168	
1-Butyne	1	0.386227	4.06049	+19.5	-347.9	57.2	0.0955511	0.0955834 ± 0.000108
	2	.388306	4.08219	+14.9	-342.9	57.2	.0955518	
	3	.366382	3.84684	+7.6	-286.2	57.2	.0956153	
	4	.386570	4.06392	-2.6	-347.6	57.2	.0955896	
	5	.387494	4.07181	-1.6	-322.4	57.2	.0955896	
	6	.394014	4.13909	-4.6	-314.2	57.2	.0956030	
2-Butyne	1	0.385354	4.09629	+5.0	-585.0	71.8	0.0948779	0.0948451 ± 0.000117
	2	.393201	4.16628	-3.5	-347.8	71.8	.0948117	
	3	.392782	4.16211	-0.6	-364.3	71.8	.0948273	
	4	.391251	4.14674	-6.5	-383.5	71.8	.0948487	
	5	.394437	4.18146	-3.2	-410.6	71.8	.0948600	
1-Butene	1	0.390078	3.92767	+4.0	-360.3	51.9	0.0998168	0.0998454 ± 0.000096
	2	.390959	3.93618	-25.8	-343.3	51.9	.0998460	
	3	.391116	3.93653	-18.6	-346.3	51.9	.0998699	
	4	.390408	3.93126	-13.5	-352.2	51.9	.0998251	
	5	.390460	3.93052	-17.6	-337.4	51.9	.0998394	
	6	.389913	3.92383	-8.8	-349.2	51.9	.0998753	
<i>cis</i> -2-Butene	1	0.391148	3.94593	+2.5	-340.9	46.2	0.0996061	0.0995839 ± 0.000200
	2	.391834	3.95409	+12.6	-316.3	46.2	.0995172	
	3	.391826	3.95239	+13.9	-332.6	46.2	.0995826	
	4	.391001	3.94650	-17.3	-343.9	46.2	.0995917	
	5	.390403	3.93893	-19.8	-364.1	46.2	.0996683	
	6	.391305	3.94849	-28.0	-332.7	46.2	.0996177	
	7	.388294	3.92211	-10.6	-352.8	46.2	.0995245	
<i>trans</i> -2-Butene	1	0.390851	3.94982	+12.5	-351.1	48.7	0.0994290	0.0994716 ± 0.000163
	2	.391170	3.95104	+12.4	-347.3	48.7	.0994730	
	3	.391794	3.95639	-9.4	-337.8	48.7	.0995162	
	4	.391341	3.95343	-13.8	-346.3	48.7	.0994974	
	5	.390536	3.94809	-12.1	-356.9	48.7	.0994426	
2-Methylpropene	1	0.393353	3.98479	+24.6	-405.8	43.0	0.0992628	0.0992089 ± 0.000171
	2	.389757	3.95268	+19.9	-412.9	43.0	.0991787	
	3	.389113	3.94302	+14.0	-389.1	43.0	.0992289	
	4	.383724	3.89059	+14.1	-382.0	43.0	.0991691	
	5	.111579	1.13195	+20.7	-174.4	43.0	.0992052	

VI. Electrical Energy Experiments

1. Procedure

The calorimetric procedure used in the electrical energy experiments was the same as in the combustion experiments [1], except that electrical energy instead of chemical energy was supplied during the reaction period. The voltage across the 65-ohm calorimeter heater was about 60 v, and the time of heating was about 20 min. (about the same length of heating time as in the combustion experiments).

2. Results of the Electrical Energy Experiments

The results of the electrical energy experiments are given in table 3, in which are listed, for the experiments on calorimeter systems I, II, and III, the following quantities: The experiment number; ΔRc , the corrected temperature rise of the calorimeter system expressed in ohms; the amount of electrical energy supplied to the calorimeter; E_s , the electrical energy equivalent of the calorimeter; and the mean value of E_s , together with its standard deviation.

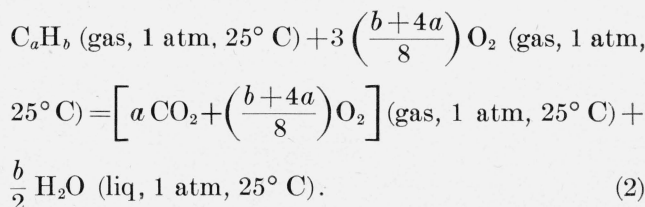
TABLE 3. The electrical calibration experiments

Calorimeter system	Experiment number	ΔRc	Electrical energy	E_s	Mean value of E_s with its standard deviation
		<i>Ohms</i>	<i>j</i>	<i>j/ohm</i>	<i>j/ohm</i>
I	1	0.401716	61953.5	154222.1	154230.2 \pm 4.3
	2	.392416	60525.4	154237.8	
	3	.391576	60397.5	154242.1	
	4	.391473	60373.0	154220.1	
	5	.391621	60399.3	154229.0	
II	1	.394433	60867.0	154315.2	154319.6 \pm 2.5
	2	.395498	61035.7	154326.2	
	3	.391968	60485.3	154311.8	
	4	.394095	60815.3	154316.3	
	5	.394425	60870.3	154326.7	
III	1	.391971	60581.3	154555.6	154562.9 \pm 3.2
	2	.395233	61086.7	154558.7	
	3	.393619	60837.8	154560.1	
	4	.393612	60839.6	154567.4	
	5	.361159	55825.4	154572.9	

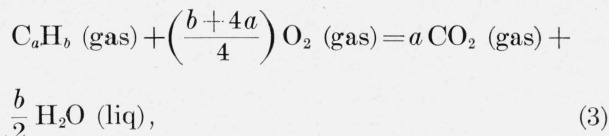
To test for systematic errors, several series of experiments were performed in which the voltage supplied across the calorimeter heater was 35 to 40 v instead of 60 v, thus making the heating period (40 to 50 min) at least twice as long as the usual 20 min. The resulting electrical energy equivalents obtained from three such experiments on calorimeter system I was $E_s = 154253 \pm 41$, from five experiments on calorimeter system II was $E_s = 154341 \pm 5$, and from five experiments on calorimeter system III was $E_s = 154568 \pm 10$ (standard deviation of the mean). Since these experiments were performed under conditions greatly different from the usual electrical energy experiments or the calorimetric combustion experiments, it was concluded that the heat leak corrections were being made properly and that the rate of stirring of the water in the calorimeter vessel was adequate.

VII. Heats of Combustion, Formation, Isomerization, and Hydrogenation

The product of B and E_s multiplied by the molecular weight of carbon dioxide and the number of moles of carbon dioxide per mole of hydrocarbon (eq 1) yields the heat of reaction as expressed by the "standard calorimetric process" [1]. In these experiments, in which approximately 50 percent of excess oxygen was employed, the process may be defined by the equation



To convert the heat of this reaction, $-\Delta Hc$, to the standard heat of combustion, $-\Delta Hc^\circ$, as expressed by the reaction at 25°C



it is only necessary to take account of the change in heat content for each gas from its given pressure to zero pressure, so that each substance will have the heat content of the thermodynamic standard state. For this calculation the change in heat content, $[H^{P=0} - H^{P=1}]_{298.16}$, was taken as -180 j/mole for the C_4 hydrocarbons, -8.1 j/mole for oxygen, and $-[8.06 + 15.9x + 17.4x^2]$ j/mole [9] for carbon dioxide-oxygen mixtures, where x is the mole fraction of carbon dioxide in the mixture. As seen from table 4, the value of this correction is -0.02 kcal/mole for each of the compounds investigated.

In table 4 are listed for each compound: the mean value of B from table 2; E_s , the mean value of the electrical energy equivalent of the calorimeter system from table 3; $-\Delta Hc$, the heat of combustion for the standard calorimetric process; $-\Delta Hc^\circ$, the standard heat of combustion; ΔHf° , the standard heat of formation; ΔH° isomerization; and ΔH° hydrogenation.

The heats of formation were calculated from the heats of combustion utilizing the values of 68.317 ± 0.010 kcal/mole [10] and 94.052 ± 0.011 kcal/mole [17] for the heats of formation of water and carbon dioxide, respectively.

The heats of isomerization are the differences in the heats of combustion, but the uncertainty is lower than the combined uncertainties of the heats of combustion since the electrical energy equivalent of the calorimeter system need not be known precisely [11]. These heats of isomerization apply to the reaction of forming the particular isomer from the first isomer listed.

TABLE 4. The heats of combustion, formation, isomerization and hydrogenation at 25° C

Compound (gas)	<i>B</i>	<i>Es</i>	-Δ <i>H</i> c		-Δ <i>H</i> c°	Δ <i>H</i> f°	Δ <i>H</i> ° iso- rization	Δ <i>H</i> ° hydro- genation
	<i>Ohms/gCO₂</i>	<i>j/ohm</i>	<i>kJ/mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>	<i>kcal/mole</i>
1,3-Butadiene.....	0.0935614 ± 0.000220	154230.2 ± 8.6	2540.26 ± 0.75	607.14 ± 0.18	607.16 ± 0.18	+26.00 ± 0.19	0	-56.37 ± 0.24
1,2-Butadiene.....	.0955293 ± 0.000108	154230.2 ± 8.6	2593.69 ± 0.55	619.91 ± 0.13	619.93 ± 0.13	+38.77 ± 0.14	+12.77 ± 0.18	-69.14 ± 0.20
<i>n</i> -Butane.....	.1059307 ± 0.000108	154230.2 ± 8.6	2876.09 ± 0.63	687.40 ± 0.15	687.42 ± 0.15	-30.37 ± 0.16	0	0
2-Methylpropane....	.1056143 ± 0.000064	154230.2 ± 8.6	2867.50 ± 0.48	685.35 ± 0.11	685.37 ± 0.11	-32.42 ± 0.13	-2.05 ± 0.12	0
1-Butyne.....	.0955834 ± 0.000216	154319.6 ± 5.0	2596.66 ± 0.85	620.62 ± 0.20	620.64 ± 0.20	+39.48 ± 0.21	0	-69.85 ± 0.25
2-Butyne.....	.0948451 ± 0.000234	154319.6 ± 5.0	2576.60 ± 0.97	615.82 ± 0.23	615.84 ± 0.23	+34.68 ± 0.24	-4.80 ± 0.28	-65.05 ± 0.28
1-Butene.....	.0998454 ± 0.000192	154562.9 ± 6.4	2716.72 ± 0.76	649.31 ± 0.18	649.33 ± 0.18	-0.15 ± 0.19	0	-30.22 ± 0.23
<i>cis</i> -2-Butene.....	.0995869 ± 0.000400	154562.9 ± 6.4	2709.69 ± 1.23	647.63 ± 0.29	647.65 ± 0.29	-1.83 ± 0.30	-1.68 ± 0.32	-28.54 ± 0.33
<i>trans</i> -2-Butene.....	.0994716 ± 0.000326	154562.9 ± 6.4	2706.55 ± 0.97	646.88 ± 0.23	646.90 ± 0.23	-2.58 ± 0.24	-2.43 ± 0.26	-27.79 ± 0.27
2-Methylpropene....	.0992089 ± 0.000342	154562.9 ± 6.4	2699.40 ± 1.04	645.17 ± 0.25	645.19 ± 0.25	-4.29 ± 0.26	-4.14 ± 0.28	-28.13 ± 0.27

The heats of hydrogenation were derived from the heats of combustion of the compounds involved, combined with the heat of formation of water. These heats of hydrogenation apply to the reaction of hydrogenation of the particular unsaturated compound to form the parent saturated hydrocarbon, *n*-butane or 2-methylpropane.

Some additional heats of isomerization, hydrogenation (or dehydrogenation), or both isomerization and hydrogenation (or dehydrogenation) are given in table 5. Hydrogen is one of the reactants (or products) if the reaction involves hydrogenation (or dehydrogenation).

TABLE 5. Heats of isomerization and/or hydrogenation in the gaseous state at 25° C

Reactant (gas)	Product (gas)									
	<i>n</i> -Butane	2-Methylpropane	1-Butene	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	2-Methylpropane	1,2-Butadiene	1,3-Butadiene	1-Butyne	2-Butyne
	Δ <i>H</i> °, kcal/mole									
<i>n</i> -Butane.....	0	-2.05	+30.22	+28.54	+27.79	+26.08	+69.14	+56.37	+69.85	+65.05
2-Methylpropane....	+2.05	0	+32.27	+30.59	+29.84	+28.13	+71.19	+58.42	+71.90	+67.10
1-Butene.....	-30.22	-32.27	0	-1.68	-2.43	-4.14	+38.92	+26.15	+39.63	+34.83
<i>cis</i> -2-Butene.....	-28.54	-30.59	+1.68	0	-0.75	-2.46	+40.60	+27.83	+41.31	+36.51
<i>trans</i> -2-Butene.....	-27.79	-29.84	+2.43	+0.75	0	-1.71	+41.35	+28.58	+42.06	+37.26
2-Methylpropane....	-26.08	-28.13	+4.14	+2.46	+1.71	0	+43.06	+30.29	+43.77	+38.97
1,2-Butadiene.....	-69.14	-71.19	-38.92	-40.60	-41.35	-43.06	0	-12.77	+0.71	-4.09
1,3-Butadiene.....	-56.37	-58.42	-26.15	-27.83	-28.58	-30.29	+12.77	0	+13.48	+8.68
1-Butyne.....	-69.85	-71.90	-39.63	-41.31	-42.06	-43.77	-0.71	-13.48	0	-4.80
2-Butyne.....	-65.05	-67.10	-34.83	-36.51	-37.26	-38.97	+4.09	-8.68	+4.80	0

VIII. Comparison with Earlier Data

The results of the present investigation are compared in table 6 with earlier data on heats of combustion and heats of hydrogenation.

TABLE 6. Comparison of the data of the present investigation with earlier data

Compound	Value from previous investigation	Value from present investigation	Difference
Standard heat of combustion, -Δ <i>H</i> c° at 25° C, in kcal/mole			
<i>n</i> -Butane.....	687.98 ± 0.17 [12]	687.42 ± 0.15	0.56 ± 0.23
2-Methylpropane....	686.34 ± 0.15 [13]	685.37 ± 0.11	.97 ± 0.19
Standard heat of hydrogenation, Δ <i>H</i> ° at 25° C, kcal/mole			
1,3-Butadiene.....	-56.56 ± 0.15 [14]	-56.37 ± 0.24	0.19 ± 0.28
2-Butyne.....	-65.19 ± 0.30 [15]	-65.05 ± 0.27	.14 ± 0.40
1-Butene.....	-30.09 ± 0.10 [16]	-30.23 ± 0.23	.14 ± 0.34
<i>cis</i> -2-Butene.....	-28.45 ± 0.10 [16]	-28.55 ± 0.33	.10 ± 0.34
<i>trans</i> -2-Butene.....	-27.41 ± 0.10 [16]	-27.80 ± 0.27	.39 ± 0.29
2-Methylpropene....	-28.11 ± 0.10 [16]	-28.14 ± 0.27	.03 ± 0.29

It is to be noted that the earlier data from this laboratory [12, 13] on *n*-butane and isobutane differ from the data of the present investigation by an amount significantly greater than the estimated uncertainty of the difference. One of the authors (Rossini) has carefully reviewed the earlier data but has been unable to discover any reason for the indicated difference other than the possibility that the earlier samples of *n*-butane and isobutane were not as pure as believed. The purity of the earlier samples of *n*-butane and isobutane was not determined from measurements of freezing points but from differential vapor-pressure measurements, quantitative evaluation of which involved assumptions as to the impurities present in the samples.

The accord of the data of the present investigation with the data on heats of hydrogenation by Kistiakowsky and coworkers [14, 15, 16] is very good, except in the case of *trans*-2-butene, for which the difference is only slightly greater than the combined uncertainties.

IX. References

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